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ABSTRACT (Maximum 200 words)

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Azo Polymers for Reversible Optical Storage. 12. Poly{1-acryloyl-4-[4-(4-nitrophenylazo)phenyl] piperazine}

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Azo Polymers for Reversible Optical Storage. 12

Poly{1-Acryloyl-4-[4-(4-Nitrophenylazo)Phenyl]

Piperazine}

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ABSTRACT

Two azo-containing vinyl monomers, 1-acryloyl-4-[4-(4-nitrophenylazo)phenyl]piperazine} (ANPP) and 1-methacryloyl-4-[4-(4-nitrophenylazo)phenyl]piperazine} (MNPP), were synthesized. MNPP did not polymerize in a few solvents, with a few free radical initiators and at a few temperatures. pANPP is amorphous with a T_g of 156 °C and decomposes above 230 °C. Birefringence can be induced by a polarized laser (514 nm) on a pANPP film to a level of 0.1 and is very stable. Comparison is made with poly{4'-[(2-(acryloyloxy)ethyl) ethylamino]-4-nitroazobenzene} (pDR1A). Biexponential curve fitting shows a lower writing rate for pANPP. Both the slow response to the laser and the higher stability of the photoinduced birefringence are due to the "rigid" piperazine linkage between azobenzene groups and backbone which prevents the azo groups from rotating freely. pANPP decomposes under long term exposure to the laser.

Key words: azo polymers · optical storage · photoinduced birefringence

INTRODUCTION

Azo-containing amorphous polymers are being studied as suitable materials for reversible optical storage¹. The photochemically induced trans-cis-trans isomerization of the azobenzene groups within the polymer is accompanied by motion of these groups. When the laser light is linearly polarized, only the

azobenzene groups which have a dipolar component along the laser polarization are activated in photoisomerization. Any azobenzene group which happens to be oriented perpendicular to the laser polarization will be inert to light. Any azobenzene group which - at the end of one of the trans-cis-trans isomerization cycles - falls on the direction perpendicular to the laser polarization will also be rendered inert. The consequence of this phenomenon is a steady increase of azobenzene groups perpendicular to the laser polarization while the laser is on. Thus, starting with an amorphous polymer film, in which the azobenzene groups are randomly oriented, linearly polarized light produces an overall orientation which can be observed either as dichroism or as birefringence. This supramolecular organization of the azobenzene groups does not generate crystalline or liquid crystalline domains; the order is not long-range². However, since the process takes place upon illumination at room temperature, below the polymer glass transition temperature, the photoinduced orientation is frozen in for an infinitely long time (after an initial relaxation upon laser termination). The orientation can be destroyed by switching to circularly polarized illumination. Circularly polarized light will activate all azobenzene groups in the plane of the film and will regenerate the thermodynamically favoured random distribution of orientation.

There are three structural factors affecting the optical behaviour of the polymer containing azobenzene groups in the side chains: the structure of the polymer backbone, the structure of the azo chromophore and the structure of the linkage between the backbone and the azo chromophore. The type of polymer backbone determines mainly some mechanical properties, such as the glass transition temperature (T_g), of the polymer. A rigid backbone may provide the polymer with high T_g that usually generates better stability of orientation in nonlinear optical (NLO) polymers, for example in some polyimides reported in the literature^{3,4}. The structure of the azo chromophore determines some properties such as the maximum absorbance, the cis-trans thermal isomerization rate as well as the orientation ability. In previous studies in this laboratory, it was found that the birefringence growth rate and the level of induced birefringence depend on the type and the size of the azo groups^{5,6}.

The linkage between azo chromophore and the polymer backbone affects both the mechanical properties (i.e. T_g) and the motion of the azo groups, thus their orientation. Although several side chain azo polymers with different spacer length have been reported for the optically induced birefringence⁷ there are no systematic studies on the linkage effect. One of the examples of the linkage effect in photonic polymers was reported by Mohlmann's group⁸. They compared different optical and

mechanical properties between two polyacrylates, one containing amino nitrostilbene linked by a six-membered ring and another containing oxy-nitrostilbene linked by a linear hexamethylene spacer, and found that the former had an approximately five times larger optically nonlinear coefficient than the later, and a higher T_g (165 °C) than the later (65 °C). This effect should be also valid for the optically induced birefringence, since the alignment of azo side groups is achieved through many cycles of trans-cis-trans isomerization and is directly related to the freedom of movement of the azo groups. One can also expect that different linkages will affect the stability of the optically induced birefringence.

We report here the synthesis of a polyacrylamide having an azobenzene side group linked through a rather rigid spacer to the main chain: poly{1-acryloyl-4-[4-(4-nitrophenylazo)phenyl] piperazine} (pANPP) and its photoisomerization and orientation behaviour. The effects of the linkage are studied by comparison with poly{4'-[(2-(acryloyloxy)ethyl) ethylamino]-4-nitroazobenzene} (pDR1A). The structures of the two polymers are shown in Scheme 1.

EXPERIMENTAL

Acryloyl chloride and methacryloyl chloride were purchased from Fluka and were distilled before use. 4-Nitroaniline and 1-phenyl piperazine were used as

purchased from Aldrich. The synthetic route for the monomers and polymer is shown in Scheme 2.

1-(4-Nitrophenylazo)phenylpiperazine

1-Phenylpiperazine (4.9 g, 0.03 mole) was dissolved in conc. HCl (20 mL) and kept below 5 °C in a ice bath. 4-Nitroaniline (4.2 g, 0.030 mole) was dissolved in conc. HCl (20 mL) by heating and the solution formed was cooled down quickly to a temperature below 5 °C with vigorously stirring to obtain a suspension. To this suspension was added sodium nitrite (2.55g, 0.030 mole) in 2 mL of water. After stirring at 0 - 5 °C for 30 min a yellow solution was obtained and added to the 1-phenylpiperazine solution slowly while stirring. The mixture was then stirred for half an hour and then was neutralized with saturated sodium carbonate aqueous solution. The product precipitated out from the solution and was collected by filtering. 7.7 g (yield 83 %) of 1-(4-nitrophenylazo) phenylpiperazine was obtained after recrystallizing the crude product from methanol, mp. 212 °C. ¹H-NMR (CDCl₃): 1.63 ppm (s, 1H, HN), 3.03 ppm (t, 4H, -CH₂-, bound to NH), 3.40 ppm (t, 4H, -CH₂-, bound to NPh), 6.95 ppm (d, 2H, aromatic, ortho to the amine group), 7.92 ppm (m, 4H, aromatic, ortho to -N=N-), 8.31 ppm (d, 2H, aromatic, ortho to NO₂).

1-acryloyl-4-[4-(4-nitrophenylazo)phenyl]piperazine (ANPP)

1-(4-Nitrophenylazo)phenylpiperazine (6.2 g, 0.020 mole) and triethylamine (2.2g, 0.022 mole) were dissolved in tetrahydrofuran (THF, 50 mL) and the solution was cooled down to about -30 °C in dry ice-acetone bath. A solution of acryloyl chloride (2.0 g, 0.022 mole) in 10 mL THF was added dropwise to the above solution with stirring. The mixture was then allowed to return to room temperature and was stirred overnight. The solid formed during the reaction was filtered off and the filtrate was evaporated giving the crude product as a red solid. The crude product was then dissolved in chloroform and washed with saturated sodium bicarbonate aqueous solution three times followed by three times washing with water. After evaporating the chloroform the product was recrystallized from THF, yield 6.2 g (yield 85 %), mp. 175 °C. ¹H-NMR (CDCl₃): 3.45 ppm (t, 4H, PhNCH₂-), 3.8 ppm (t, 4H, -CONCH₂-), 5.75 ppm (d, 1H, H₂C=, trans to =CH), 6.35 ppm (d, 1H, H₂C=, cis to =CH), 6.60 ppm (m, 1H, =CHCO-), 6.98 ppm (d, 2H, aromatic, ortho to the amine group), 7.93 ppm (m, 4H, aromatic, ortho to -N=N-), 8.33 ppm (d, 2H, aromatic, ortho to NO₂).

1-methacryloyl-4-[4-(4-nitrophenylazo)phenyl]piperazine (MNPP)

It was prepared in the same way as 1-acryloyl-4-[4-(4-nitrophenylazo)phenyl]piperazine, mp. 196 °C. ¹H-NMR (CDCl₃): 1.96 ppm (s, 3H, -CH₃), 3.41 ppm (t, 4H, PhNCH₂-), 3.78 ppm (t, 4H, -CONCH₂ -), 5.01 ppm (s, 1H, H₂C=,

trans to -CH₃), 5.26 ppm (s, 1H, H₂C=, cis to -CH₃), 6.98 ppm (d, 2H, aromatic, ortho to the amine group), 7.93 ppm (m, 4H, aromatic, ortho to -N=N-), 8.33 ppm (d, 2H, aromatic, ortho to NO₂).

DR1A and pDR1A

DR1A was synthesized by coupling acryloyl chloride and Disperse Red 1 and then polymerized with AIBN as described previously².

poly{1-acryloyl-4-[4-(4-nitrophenylazo)phenyl]piperazine} (pANPP)

ANPP (1 g) and AIBN (0.1 g) were dissolved in 10 mL dioxane, put in an ampoule, then the solution was degassed by bubbling nitrogen for 15 mins and the ampoule was sealed in vacuum. The ampoule was placed in an oil bath set at 60 °C. After 48 hours the solution was poured into 150 mL methanol. The precipitate formed was collected and dissolved in THF, then reprecipitated twice from methanol. The red solid was dried in a vacuum oven at 50 °C for 20 h. 0.7 g polymer was obtained with peak molecular weight of 23000. A solution ¹H-NMR spectrum of the polymer is shown in Figure 1.

Attempts to polymerize MNPP were made in different solvents and initiators. None of them succeeded. All polymerization experiments are summarized in Table 1.

Characterization and film preparation

The films were prepared by spin-coating from THF solution onto a glass substrate and dried in vacuum at 100 °C for 20 hr. The film thickness was in the 100 to 200 nm range as measured by interferometry. The procedure for reversibly inducing birefringence with a laser beam on the polymer film was described previously². “Writing” and “erasing” were performed using an argon laser (514 nm) of 6 mW intensity on a spot of 2 mm in diameter at room temperature. Calorimetric properties transitions were measured on a Mettler TA-30 DSC instrument equipped with a TA-3000 processor at the scan rate of 20 °C/min. The electronic spectra were recorded on a Shimadzu spectrometer. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with monodisperse polystyrene standards using a Waters Associates liquid chromatography equipped with a Model R01 differential refractometer and Model 440 absorbance detector. THF was used as the eluent. The ¹H-NMR spectra were obtained on a Bruker AC-F 200 NMR spectrometer in deuteriochloroform solution.

RESULTS AND DISCUSSION

Polymerization

Both the acrylamide and the methacrylamide were synthesized with good yields. ANPP polymerizes easily with AIBN in dioxane at 60 °C. pANPP is soluble in common solvents such as THF and chloroform. The film of pANPP has a

maximum electronic absorbance at about 433 nm as shown in Figure 2 (curve A). The wavelength is close to the absorbance of pDR1A which is about 458 nm (this wavelength has been reported for the corresponding methacrylate polymer)⁶. pANPP films are amorphous as proven by polarized microscopy. The DSC curve of the polymer shows a glass transition temperature at 156 °C and decomposition at about 230 °C.

Unlike ANPP, MNPP does not polymerize under the described conditions. The inability of MNPP to polymerize may be due to the steric hindrance between the methyl group and the carbonyl group on the same carbon of the double bond. This effect was also found in some other N-disubstituted methacrylamides such as N,N-dimethyl methacrylamide^{9,10}.

Photoinduced birefringence

A typical “writing-relaxation-erasing” curve obtained when subjecting a pANPP film to illumination with a 514 nm “writing-erasing” laser beam and using a 674 nm “reading” laser beam at room temperature is shown in Figure 3. The birefringence is rapidly induced when the linearly polarized laser beam is turned on at point A and reaches a saturated level. The birefringence relaxes at point B, where the writing beam is turned off, and reaches a stable level before point C. The induced birefringence is then eliminated by turning on the same laser, but circularly

polarized, at point C. The maximum value of the photoinduced birefringence is about 0.10, which is slightly higher than the maximum birefringence achieved in a typical azo polymer, pDR1A (0.08)¹¹. This is remarkable, when one considers that the absorptivity of a pANPP film at the laser wavelength is about half of the absorptivity of a pDR1A film ($2.7 \times 10^{-6} \text{ m}^{-1}$, compared to $4.7 \times 10^{-6} \text{ m}^{-1}$) and, normally, the higher the absorbance the higher the induced birefringence. The explanation may be related to the structural differences between the two polymers, mainly the different linkage between the azo chromophore and the polymer backbone. The lower mobility of the azo groups in pANPP due to the more rigid six-membered ring link, probably increases the population of oriented azo groups by reducing the probability of thermal randomization.

To describe the growth of the photoinduced birefringence and its relaxation, expressions for curve fitting have to be found⁶. Both the growth and the relaxation of the photoinduced birefringence are complex processes, involving some photochemical processes (isomerization) and some motional ones (orientation and reorientation), and the simplest fitting can be done by approximating with biexponential curves. This biexponential approximation was found to be satisfactory for most of the azo homopolymers, and even for some copolymers, but was inadequate when two types of azobenzene groups were bound to the same main

chain¹². For pANPP and pDR1A, the birefringence growth can be fitted very well by a biexponential equation. Equation (1) is used to fit the birefringence growth (A to B in Figure 3)⁶:

$$\Delta n = A \cdot \{1 - \exp(-k_a \cdot t)\} + B \cdot \{1 - \exp(-k_b \cdot t)\} \quad (1)$$

where Δn represents the birefringence achieved at time t , k_a and k_b are the time constants for birefringence growth, and A and B are constants. The sum of A and B represents the maximum induced birefringence, and the normalized A and B (A_n and B_n respectively) represent the contribution of each of the two terms to the induced birefringence. The fitting parameters for Equation (1) are listed in Table 2. The interpretation of the biexponential process is usually done by looking separately at a fast process and at a slow process. The time constants in Table 2 (k_a and k_b) indicate that the fast process is about 20 times faster than the slow process for both pANPP and pDR1A. The contribution to the birefringence by the fast process (A_n) is more important than the contribution of the slow process (B_n), again for both homopolymers. As reported previously, the fast process is probably dominated by the isomerization rates and the local mobility of the azo groups, and the slow process depends on the coupling interaction between the azo group and the polymer segments and on the mobility of the polymer segments. The main difference between pANPP and pDR1A in the birefringence growth is in the actual rates of

growth, both k_a and k_b being smaller in pANPP than in pDR1A. The main structural difference between pANPP and pDR1A, as mentioned above, is the type of linkage between the azo moieties and the polymer backbone. The mobility of the azo groups in pANPP is reduced because the more rigid link of the piperazine structure prevents one of the azobenzene rings from freely rotating as the other does, and this probably affects the magnitude of the k_a constant. As a result, it takes longer to orient the azobenzene group in pANPP than in pDR1A. The main chain motion is also expected to be reduced by the rigid linkage, and this is clear when comparing the T_g of pANPP (156 °C) with the T_g of pDR1A (91 °C)². The difference in the main chain mobility probably affects the magnitude of the k_b constant. Therefore, the difference in linkage between the azobenzene group and the main chain appears to have an effect on both the fast and the slow processes involved in the photoinduced birefringence growth.

The relaxation curve (B to C in Figure 3) can similarly be fitted with a biexponential equation as follows⁶

$$\Delta n_r = C \cdot \exp(-k_c \cdot t) + D \cdot \exp(-k_d \cdot t) + E \quad (2)$$

where Δn_r is the relaxed birefringence at time t after turning off the “writing” laser, k_c and k_d represent the time constants of the birefringence relaxation for the two kinds of processes, C and D are the constants reflecting the contribution of the

two processes to the birefringence relaxation and E is the final birefringence independent on time. The sum of normalized C and D (C_n and D_n respectively) describes the fraction of birefringence lost and the normalized E (E_n) represents the fraction of stable birefringence. The two processes here are also assigned to some motions of the azo groups, including thermal cis-trans isomerization (the fast process) and to motions involving the main chain (the slow process). The fitting results are listed in Table 2. Comparing these results with those for pDR1A obtained in the same conditions it is obvious that the stable birefringence (E_n) is much larger for pANPP than for pDR1A although their relaxation rates are similar. The higher stability of the photoinduced birefringence for pANPP can be explained by structural differences between pANPP and pDR1A. The benzene rings at both ends of the azo group in pDR1A may rotate freely around the azo bond since there is a spacer between the azo chromophore and the backbone. One of the benzene rings of pANPP is blocked by the piperazine ring (double linkage) so that its freedom of rotation around the azo bond is probably reduced. As a consequence, the induced alignment level of the azo groups in pANPP is more stable than in pDR1A. This kind of steric effect is similar to previous observations in another azo polymer, poly{4, 4'-(1-methylethylidene) bisphenylene 3-[4-(4-nitrophenylazo)phenyl]-3-azapentanedioate} (pMNAP)¹, shown in Scheme 3. One of benzene rings of the azo

group in pMNAP is connected to the main chain by two bonds, instead of the one present in pDR1A, for example, decreasing the motional freedom of the azo group; therefore, the stability of the birefringence induced in the film is higher than that of pDR1A. Again, the higher T_g caused by the rigid linkage could also be a reason for the better stability. The T_g of pMNAP is very similar to the T_g of pANPP (152°C)¹.

A multiple “writing” and “erasing” on a pANPP film was performed at room temperature. The same birefringence levels were reached for every cycle (Figure 4) as was found in all other azo polymers studied such as pDR1A². When the film was exposed to a laser for 72 hours, however, the birefringence of pANPP film decayed to almost zero and a FT-IR spectrum of the exposed film showed clear changes (Figure 5). The absorbance band of the azo bond at 1383 cm^{-1} and a band of amino substituted benzene at 1228 cm^{-1} (Figure 5-A) disappear after exposure (Figure 5-B). This indicates that the azobenzene structure is destroyed. The change is also found in the electronic spectrum (Figure 2) where the maximum absorption wavelength shifts from 433 nm to 357 nm. Although the exact mechanism of the decomposition is not clear, it is likely that the photoinduced decomposition is related to the existence of the amide group and the cyclic piperazine unit since it was not observed in other polymers with ester bonds studied in our laboratory. A thermal decomposition of a polyimide with a piperazino benzoic amide structure

similar to ANPP was reported by Miller and co-workers¹³. The poor thermal stability was attributed to the presence of the cycloalkyl substituent.

CONCLUSIONS

ANPP and MNPP were synthesized. Their free radical polymerization was attempted. MNPP does not polymerize in common conditions probably due to the steric hindrance. pANPP can be obtained by solution free radical polymerization. It has a glass transition temperature of 156 °C. The film of pANPP shows a fairly stable photoinduced birefringence level. The maximum birefringence achieved on a pANPP film is slightly higher than on pDR1A in similar conditions. Biexponential curve fitting shows lower writing rates for pANPP. Both the slower response to the laser and the higher stability in comparison to pDR1A are explained by the presence of more rigid linkage between the azobenzene groups and the main chain, which prevents the free rotation of the aromatic rings around the azo bond. The photo decomposition of pANPP under long term exposure to a laser may limit its use as a material for optical storage.

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14. Figure captions

Figure 1. ^1H NMR spectrum of pANPP in CDCl_3 at room temperature.

The assignments are given on the spectrum.

Figure 2. Electronic spectra of pANPP film before (A) and after (B) 72 hrs exposure to the laser.

Figure 3. "Writing-erasing" curve of a pANPP film. At point A the linearly polarized laser ("writing" beam) is turned on; at point B the "writing" beam is turned off; at point C the circularly polarized laser (erasing beam) is turned on.

Figure 4. Multiple "writing-erasing" on the film of pANPP at room temperature. At point A the linearly polarized laser ("writing" beam) is on; at point B the laser is switched from "writing" to "erasing" (circularly polarized laser). At point C the laser is switched from "erasing" to "writing" again. From A to C or From C to the next C is a "writing-erasing" circle.

Figure 5. FT-IR spectra of pANPP film before (A) and after (B) 72 hrs exposure to the laser.

Table 1. Polymerization of ANPP and MNPP

Monoimers	Solvent	Initiator	Temperature, °C	Time, hr	polymer [§]
MNPP	dioxane	AIBN	60	48	—
MNPP	dioxane	BPO ‡	80	72	—
MNPP	THF	AIBN	60	48	—
MNPP	acetic acid	AIBN	60	48	—
ANPP	dioxane	AIBN	60	48	+

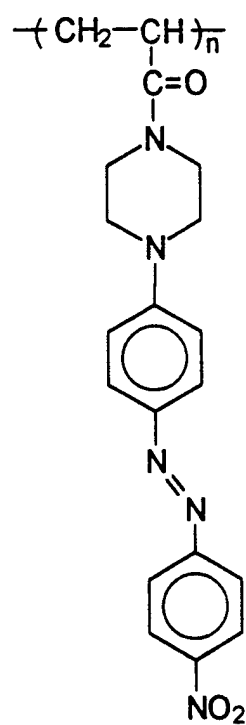
‡ benzoyl peroxide

§ — : no polymer obtained; +: polymer obtained

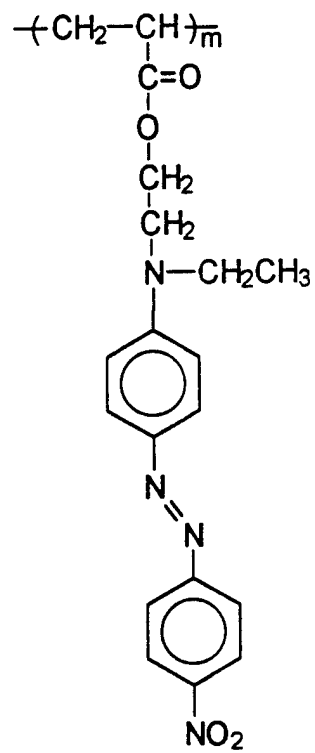
Table 2. The biexponential curve fitting for Equation (1) and Equation (2)

Fitting Parameters	pANPP	pDR1A
A_n^*	0.85 ± 0.02	0.85 ± 0.01
B_n^*	0.15 ± 0.02	0.15 ± 0.01
C_n^*	0.02 ± 0.01	0.11 ± 0.01
D_n^*	0.02 ± 0.01	0.11 ± 0.01
E_n^*	0.96 ± 0.02	0.78 ± 0.01
k_a	2.2 ± 0.4	4.1 ± 0.1
k_b	0.09 ± 0.03	0.22 ± 0.03
k_c	1.7 ± 0.6	1.5 ± 0.2
k_d	0.09 ± 0.01	0.07 ± 0.01

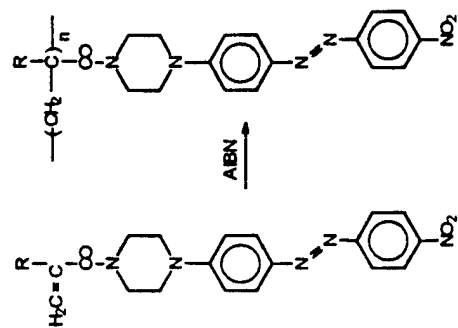
* $A_n = A/(A+B)$; $B_n = B/(A+B)$; $C_n = C/(C+D+E)$; $D_n = D/(C+D+E)$; $E_n = E/(C+D+E)$.



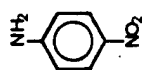
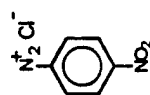
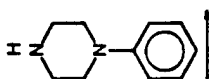
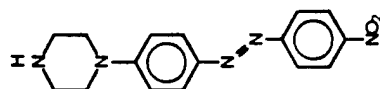
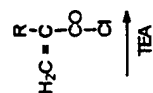
pANPP



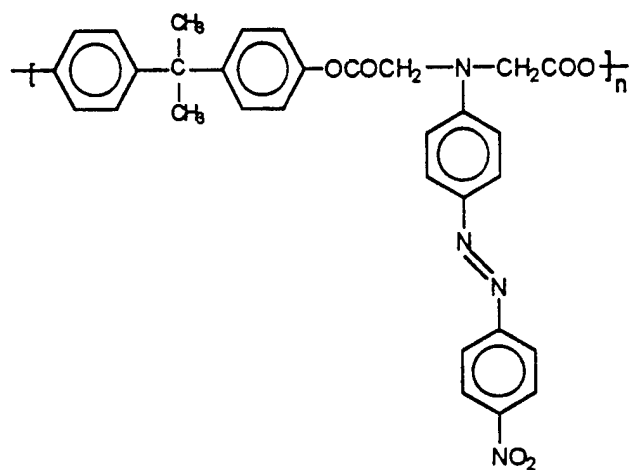
pDR1A



$\text{R} = \text{H (ANPP)}$
 $\text{CH}_3 \text{ (MPP)}$

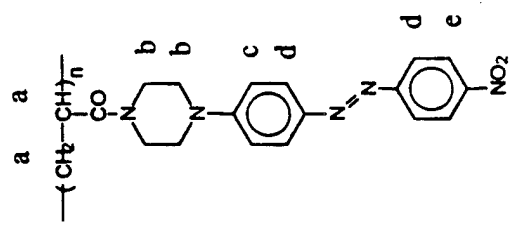


A. Natansohn *Scheme 2*



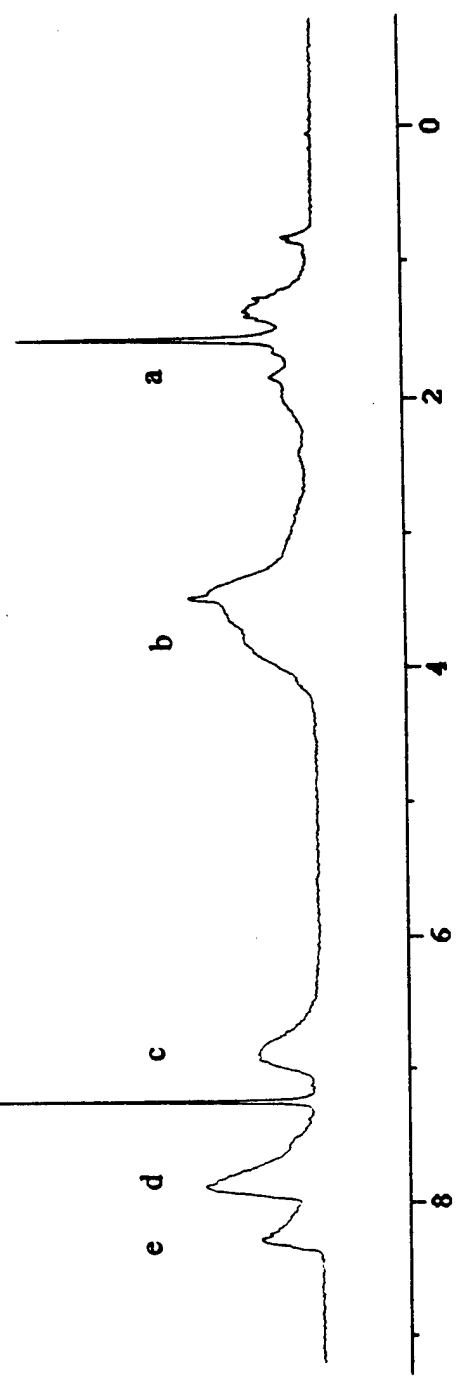
pMNAP

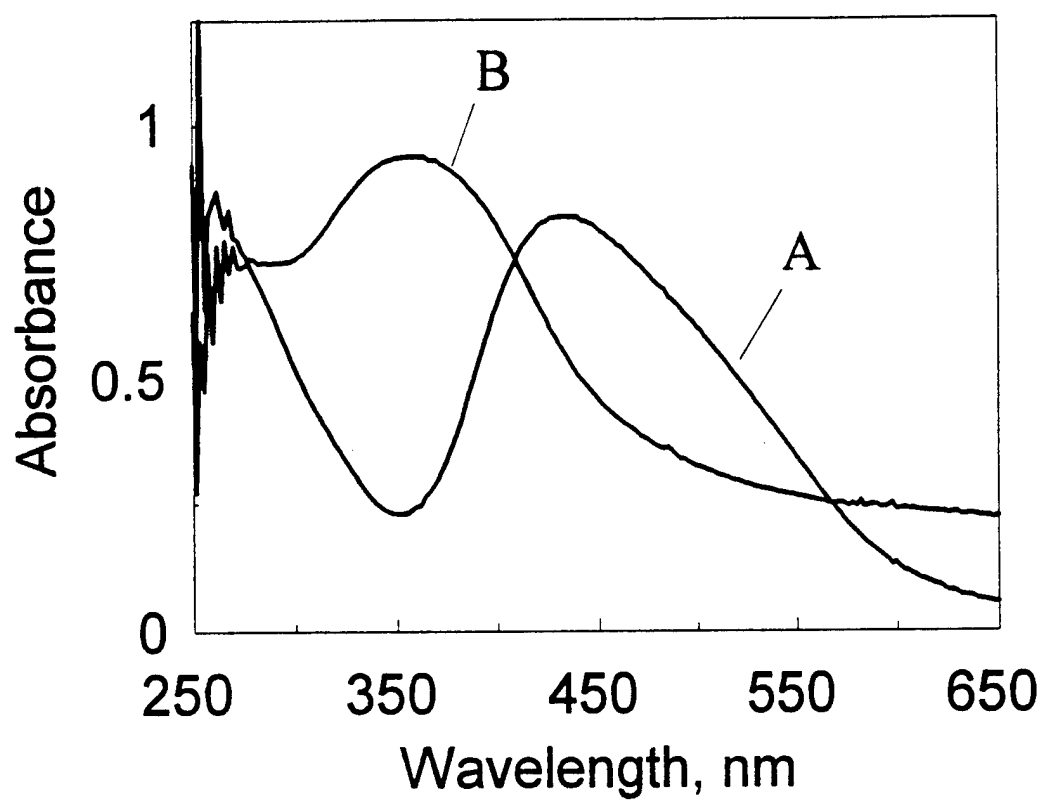
A. Natanson Scheme 3



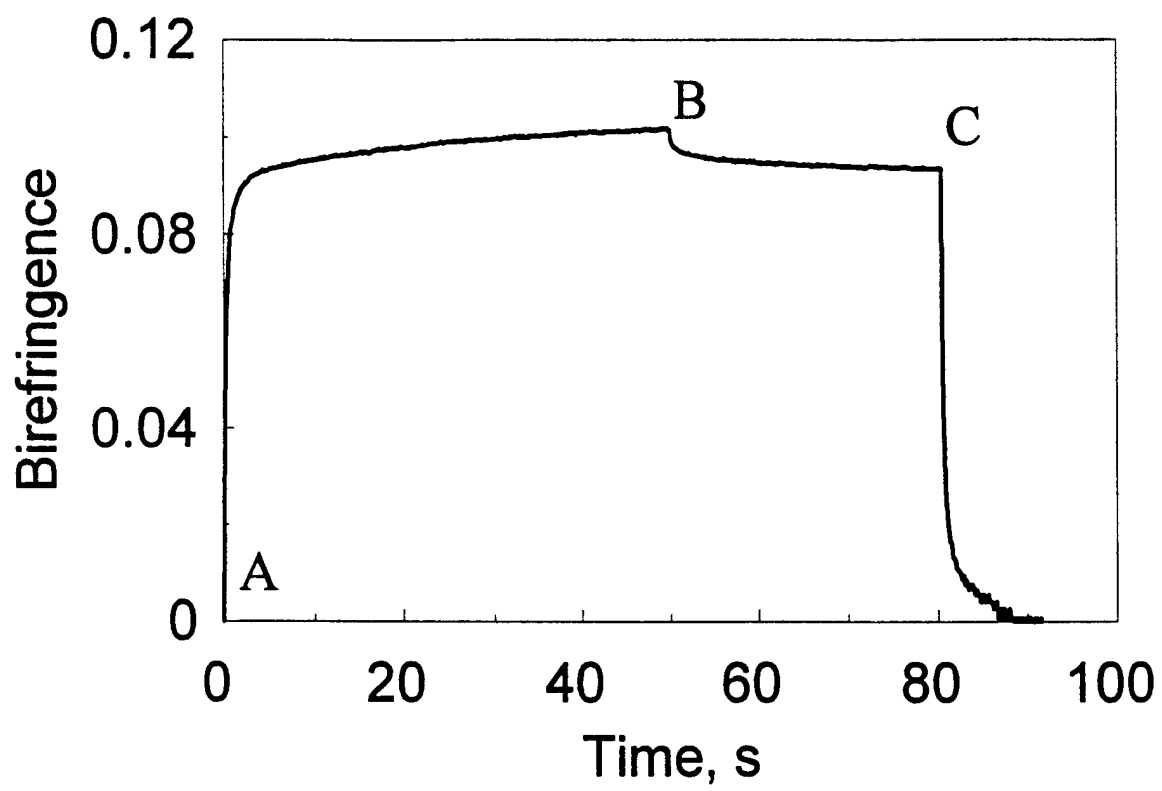
CHCl₃

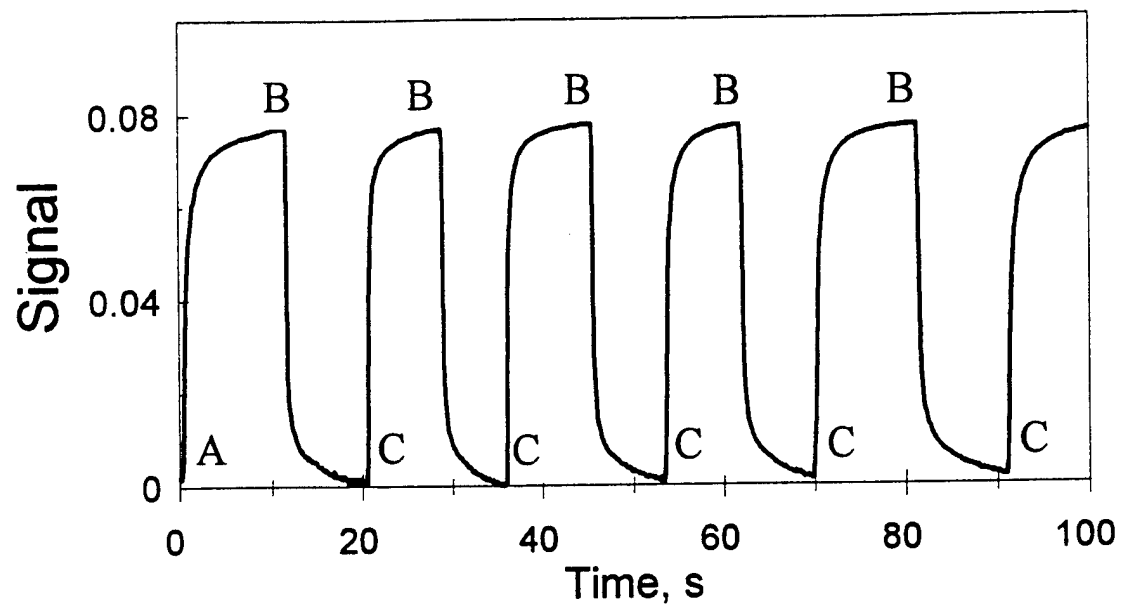
H₂O

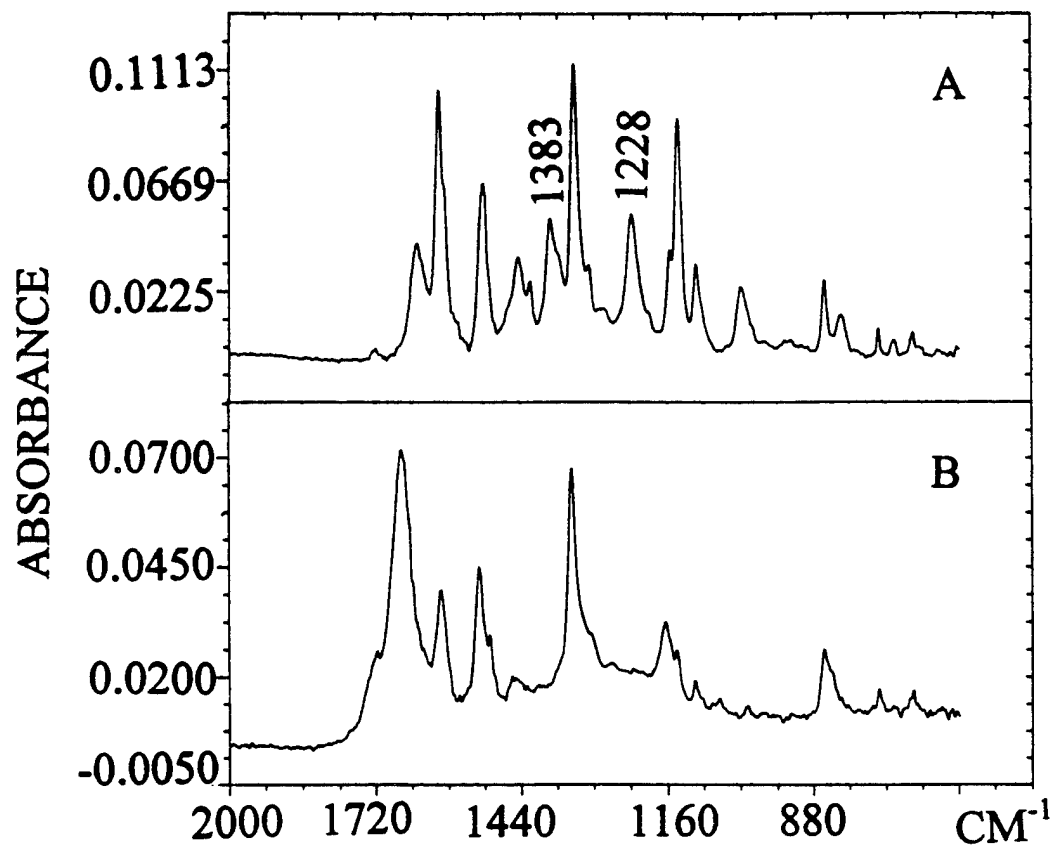




A. Natansohn Fig. 2







A. Natansohn Fig. 5